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DEVELOPMENT OF LOW-MELTING GLASSES FOR DECORATING FACING MATERIALS

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The compositions of low-melting glasses based on the sodium-borosilicate system are developed. It effect of the composition on the thermal properties of the glasses is studied. It is shown that the wastes from electrochemical production processes can be used instead of the conventional raw materials. Testing under natural conditions showed that the glasses have good wettability with respect to concretes and that colored glasses can be used to decorate concretes.

Key words: low-melting glass, pigments, decoration, facing material, utilization of wastes.

Colored low-melting silicate glasses are synthesized on the basis of compositions containing lead oxides or a large quantity of boron oxide and are characterized by low reproducibility and high cost. The high volatility of these oxides during glassmaking requires special filters to be installed in order to protect the environment.

We have performed work on developing low-melting glasses that do not contain lead oxide. The molar composition of boron oxide does not exceed 20%. The glasses developed are suitable for obtaining coatings on facing materials such as pearlite-phosphate and asbestos cement as well as on a plate made using wastes from the production of cellular concrete.

One of the most important conditions for obtaining a high-quality glass coating on concrete is that the CLTE of the substrate must match that of the coating. The difference between the CLTEs must not exceed 8 – 10 units.

To determine the thermal characteristics of foam concrete and heavy concrete, these materials were used to make $4 \times 4 \times 50$ mm ground molding by means of the well-known technology. Since the concretes have a porous structure, it is natural to assume that during mechanical working the surface of the concrete absorbs some moisture, so that before measurements began the samples were dried in a dessicator at temperature 50 – 70°C for 2 – 3 h.

The thermal properties of the samples were determined in conformance with GOST 10978–93 on a DKV-4 quartz dilatometer in the temperature range 20 – 900°C.

The study of heavy concrete revealed the following. In the temperature interval 20 – 520°C the CLTE varies over the range $(43 - 71) \times 10^{-7}\ K^{-1}$; in the interval 520 – 570°C the CLTE equals $297 \times 10^{-7}\ K^{-1}$; and, in the interval 570 – 592°C the CLTE assumes its maximum value of $320 \times 10^{-7}\ K^{-1}$, after which as temperature increases it decreases and becomes negative, equal to $-238 \times 10^{-7}\ K^{-1}$ in the temperature range 860 – 900°C (Table 1).

In determining the CLTE of foam concrete, the initial effect of the temperature is to decrease the coefficient to negative values ($-237 \times 10^{-7}\ K^{-1}$) in the temperature interval 20 – 200°C. Then, it gradually increases, reaching is maximum positive value ($224 \times 10^{-7}\ K^{-1}$) in the interval 577 – 600°C. Next it decreases, once again becoming negative and assuming its minimum value ($-11{,}703 \times 10^{-7}\ K^{-1}$) in the interval 772 – 829°C. This complex behavior of the dilatometric curve is explained by the porosity, shrinkage, and structure of the material (Table 2).

The effect of preliminary heat treatment (calcination) on the wettability of the substrate surface by a water suspension of CMC (carboxymethyl cellulose) and glass powder was investigated. It was found that the structure of foam concrete remains practically unchanged while that of heavy concrete becomes more porous. This explains the immediate absorption of water by the surface of heavy concrete.

Matrix-phase glasses were synthesized in the sodium-borosilicate system. Founding was performed in 1-liter quartz crucibles in gas and electric furnaces with different atmospheric conditions. The founding temperature was 1250 ± 20°C with 1-h soaking at the maximum temperature. Firing was conducted in an electric muffle furnace for 1.5 h

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TABLE 1. Temperature Dependence of the CLTE of Heavy Concrete

Temperature interval, °C	CLTE, 10^{-7} K^{-1}	Temperature interval, °C	CLTE, 10^{-7} K^{-1}
20 – 100	45	570 – 580	146
20 – 200	44	580 – 592	320
100 – 200	43	594 – 620	34
100 – 230	43	620 – 644	5
230 – 300	70	644 – 720	– 38
300 – 420	71	720 – 790	– 57
420 – 520	55	790 – 860	– 95
520 – 570	297	860 – 900	– 238

TABLE 2. Temperature Dependence of the CLTE of Foam Concrete

Temperature interval, °C	CLTE, 10^{-7} K^{-1}	Temperature interval, °C	CLTE, 10^{-7} K^{-1}
20 – 74	5	577 – 600	224
74 – 140	– 172	600 – 609	73
140 – 200	– 237	609 – 658	4
200 – 270	– 196	658 – 666	– 49
270 – 320	– 123	666 – 706	– 162
320 – 390	– 161	706 – 740	– 520
390 – 480	– 85	740 – 756	– 753
480 – 538	– 48	756 – 772	– 2523
538 – 577	5	772 – 829	– 11,703

at temperature 530 ± 20°C. The glasses were used to make samples for investigating the physical-chemical properties, such as the CLTE, fusion and flow temperatures, and the crystallization proneness of the glasses as function of the composition.

The fusion temperature of the glasses lies in the range 650 – 700°C, and the CLTE varies over the range (70 – 110) × 10^{-7} K^{-1} depending on the content of the modifying oxides.

Decreasing the barium oxide content in the glass and at same time increasing the magnesium oxide content decreases the fusion temperature of the glasses with the CLTE increasing by a negligible amount. However, complete replacement of barium oxide with magnesium oxide increases the proneness of the glasses to crystallization, while for molar content of magnesium oxide in the glass above 25% complete crystallization occurs.

In the course of this work, the possibility of using wastes from electrochemical production processes and the production of printing plates, specifically, spent solutions of galvanic baths, as a replacement for the conventional raw materials during synthesis was investigated.

Solutions based on copper chloride are used for etching printing plates in the production of radio apparatus. For example, the spent acidic etchant RZ-1 contains the following (g/liter): copper chloride 200 – 250, ammonium chloride 100 – 140, HCl 50 – 60, and H_2O 15 – 30. The copper – ammonia etchant RZ-2 contains (g/liter): $CuCl_2$ 100 – 110; ammonium chloride 150 – 250, and ammonium carbonate 20 – 30. The average quantity of spent solutions is 200 tons/yr per plant. The amount of the solution RZ-3 containing iron and copper chlorides is approximately 30 tons/yr. These wastes are not salvaged. Only about 10% of the copper-containing wastes are reprocessed; they are precipitated on electrodes to increase the extraction of metallic copper.

Solid substances were obtained from these solutions by two methods: evaporation and precipitation using a 1 N solution of sodium hydroxide followed by filtration of the residue. In the course of the precipitation process the precipitate was separated at solution pH ~ 9. The solutions were filtered and dried. The solid substance obtained was investigated by x-ray phase analysis, which showed the presence of copper chloride crystals in the RZ-1 and RZ-2 wastes as well as iron chloride and copper crystals in RZ-3 waste. The materials obtained by precipitation are enriched with sodium oxide. The method used to separate the solid residue by precipitation is best for use in radio works.

The solid components obtained were used as raw materials for forming mixes by the conventional method, taking account of the form and concentration of the salts of the elements present in the precipitate obtained from solution.

Mixtures were also tested (content in %[3] referred to dry matter): CaO 50 – 65 and pigments — about 8 CuO, 20 – 30 Fe_2O_3, and small additions of manganese and chromium oxides.

The RZ-4 waste obtained from a manufacturing plant has a moisture content of about 30% and can be easily dried in air. A series of glasses was made using these wastes. The material was introduced in the amounts 1 – 7% (above 100%) into the matrix composition of the glasses. The temperature parameters for glassmaking and firing remained the same as for matrix-phase glasses.

The synthesized glasses were light blue and green with different color intensity, depending on the content of the wastes introduced. The light transmission of the samples in the visible range of the spectrum was determined on 2-mm thick polished plates cut from the glasses; it was found that two peaks were present — at wavelengths 400 and 450 nm for RZ-4 wastes and one peak at 470 nm for RZ-1. For 7% (above 100%) RZ-4 waste introduced, the glass acquires a red color as a result of additional heat treatment in the temperature range 630 – 700°C and the reduction of copper by the components present in the glass composition. It should be noted that no additional reducing agents, specifically, expensive and allocated pure tin oxide and carbon, both of whose presence in the glass is a necessary condition for obtaining copper ruby, were used in synthesizing the glasses. All

[3] Here and below — content by weight.

glasses synthesized using the wastes indicated above are low-melting. Fusion of the boundaries of the samples starts in the temperature interval 630 – 650°C, terminating with complete spreading of the glasses in the interval 780 – 800°C.

The study of the physical-chemical, optical, and technological properties of the glasses showed that the solid wastes can be used instead of the conventional components. Thus, materials containing transition-element oxides can be used instead of expensive and scarce pigments for coloring glasses to be used in construction and technology.

Glass synthesized using the wastes indicated were tested for decorating facing materials. The substrates consisted of plates made of pearlite-phosphate and asbestos cement as well as plates obtained using wastes from the production of cellular concrete. The coatings were deposited as follows: glass powder was mixed with organic binder and deposited on the surface of the facing plate, after which the samples were placed in a firing furnace at a prescribed temperature. Provided that the CLTE of the glass matches that of the substrate, coatings with a smooth surface with no spotting can be obtained. The CLTE was adjusted primarily by changing the content of the alkali-earth oxides in the glass compositions.

This system can be used to obtain glasses which are transparent as well as opalescent and opacified by liquation of the glasses. A small quantity of a pigment combined with adjustment of the basicity of the glasses makes it possible to vary the color over a wide range.

The use of wastes for coloring coatings will make it possible to lower the cost of architectural-construction materials as well as to increase the color range of building facades. Using glass prone to the reduction of copper for coatings makes it possible to obtain different decorative effects, since copper becomes distributed in the glass nonuniformly; marbled coatings can be obtained by increasing the copper content in the glass and “adjusting” sections of opacified glass so as to form “liver.”

The glass developed can be recommended for decorating facing materials used for interior and exterior finishes.

The adopting of the glasses developed will aid in protecting the environment and serve to create a waste-free technology while decreasing the cost of glass coatings and making it possible to develop new facing materials with a wide range of colors.